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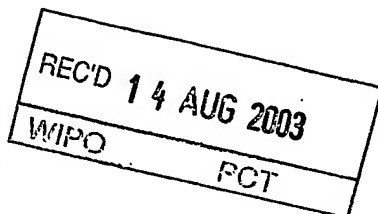


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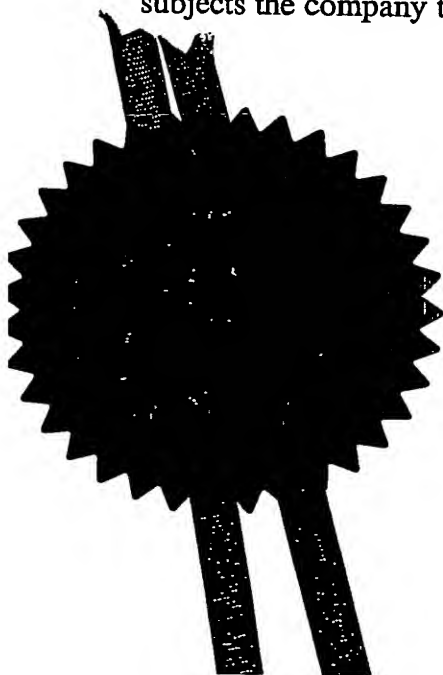


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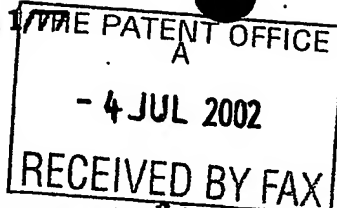
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MC 1598 GB

2. Patent application number

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0215384.9

- 4 JUL 2002

3. Full name, address and postcode of the or of each applicant (underline all surnames)

(1) Johnson Matthey Public Limited Company
2-4 Cockspur Street, Trafalgar Square, London SW1Y 5BQ(2) Aubin Limited
Unit 1 Castle Street, Castlepark Industrial Estate,
Ellon AB41 9RF, Scotland

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

(1) GB

(2) Scotland

536268007

8255788002

4. Title of the invention

IMPROVEMENTS IN METAL SALTS

5. Name of your agent (if you have one)

IAN CARMICHAEL WISHART

"Address for service" in the United Kingdom to which all correspondence should be sent (excluding the postcode)

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8256331001

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Country

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Number of earlier application

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(day / month / year)

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11.

I/We request the grant of a patent on the basis of this application.

Signature

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Date 4 July 2002

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DUPLICATE

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IMPROVEMENTS IN METAL SALTS

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The present invention concerns improvements in metal salts, more especially concerns the removal of certain ions from aqueous solutions.

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It is commonplace in drilling for oil and gas, to use fluids such as brines as well servicing fluids. In general, such fluids have desirably a high density. In particular, highly concentrated alkali metal salts of carboxylic acids have been developed for use in oil and gas well drilling and completion operations. Such a fluid may be based upon cesium salts such as cesium formate, which can provide brines of specific gravity values of 1.8 to more than 2.1, depending upon solution concentrations.

15

During use of such brines, they may be contaminated with sodium chloride from sea water or from water or salt entrained within the rock and mud during application in the well bore. Chloride ions can cause severe corrosion of steel pipework and additionally may be incompatible with the rock matrix, causing damage to the near well bore area. Such problems may result in users of such brines refusing to re-use chloride-contaminated brines. A charge of cesium formate solution for use as an oil field brine may cost in the order of \$10M, so there is considerable need to improve the prospects for recycling such a brine.

25

Further, if a diluted brine is returned to high density by evaporation of water, any chloride concentration will increase by this process, thereby rendering the brine less suitable to use.

30

Accordingly, this invention can be applied to removal of chloride from brine both caused by contamination in use or caused by a concentration process such as evaporation, and throughout this description and claims the term "recovered brine" is to be understood as including brines which have been concentrated..

The present invention provides a method of treating an alkali metal carboxylate salt brine contaminated with chloride ion, comprising mixing such contaminated brine with a

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solution of a silver salt, especially silver nitrate, causing silver chloride to be formed and separating the silver chloride from the residual brine.

The invention may also be expressed as a method of use of an alkali metal
5 carboxylate salt brine, comprising the recovery of used brine contaminated with chloride
ion, treating the recovered brine with a solution of a silver salt, especially silver nitrate,
causing silver chloride to be formed and separating the silver chloride from the brine, and
re-using the brine. Desirably, the brine comprises cesium as the alkali metal, and formate,
acetate or other species, as the salt anion. The brine may comprise mixtures of alkali metal
10 carboxylates. Further, the brine may comprise one or more polymers or other components
which are adjuvants and provide desirable properties to the brine or avoid disadvantages.

The preferred silver salt is silver nitrate, and for ease of description, all references
hereinafter will be to silver nitrate.

15

Since the specific gravity of the brine is extremely important, it is desirable to
minimise any loss of specific gravity by undue dilution during the treatment. Accordingly,
it is desirable to use silver nitrate solutions containing at least 200g/l of AgNO_3 , more
preferably at least 300g/l AgNO_3 and most preferably at least about 950g/l. At room
20 temperature, saturation concentrations are about 1400g/l AgNO_3 . The silver nitrate solution
may contain other components which do not significantly adversely interfere with the
method of the invention, or the performance of the brine. The silver nitrate solution is
conveniently a product stream from a process involving the manufacture of high purity
silver nitrate. This can provide economies arising from heat and water savings and other
25 processing costs.

The treatment of the invention is conveniently carried out at room temperature, but
may be carried out at ambient temperature. It will be borne in mind that solubility decreases
with decreasing temperature, and crystallisation may occur. Allowing the brine to cool to
30 ambient temperature, or preferably cooling to about 0°C , facilitates the removal of sufficient

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cesium nitrate formed as a by-product to create a stable solution that can be supplied and used in winter conditions.

Conveniently, silver chloride may be removed from the brine by filtration. This is particularly applicable because of the relatively high value of the silver chloride. Other methods for separation may be used, however, such as hydrocyclones or centrifuges, and where applicable or desirable, polymeric materials may be added to enhance separation.

The treatment may be carried out in a two-step process, or, in a preferred embodiment, in a single step process. Desirably, at least a stoichiometric quantity of silver nitrate is used, relative to chloride ion, in the treatment. More desirably, the quantity of silver nitrate is from approximately 105% to approximately 115% stoichiometric, especially from 108 to 112% stoichiometric, for brines containing 13.5g/l chloride. If the brine has other chloride contents, the stoichiometric uplift may differ and can be established by trial and error.

The recovered silver chloride may carry entrained by-products such as silver formate and cesium nitrate. Under preferred conditions, these are minimised and removed to permit the production of a re-usable brine. By washing and crystallisation, silver chloride crystals may be obtained and the silver value recovered in conventional ways by conversion to other compounds or silver metal, using methods available to the person of ordinary skill in the art. In general, therefore, it is preferred to separate the silver chloride by filtration, but conventional washing of the solids is not desirable if it causes undue dilution of the filtrate. Entrained cesium formate in the filtered precipitate may be washed out subsequently, using water, and cesium nitrate may also be recovered if desired.

The skilled person may use the information herein to optimise the process, using conventional techniques.

The invention may be further understood with reference to the following Examples.

EXAMPLE 1**Stoichiometric Additions of AgNO₃**

200 ml samples of a used cesium formate brine, containing 1587g/l cesium formate, 13.53g/l chloride, 0.720wt% sodium and 2.63 wt% potassium were used for all tests described. Desirably, the chloride level will be reduced below 1g/l, more preferably 0.3 - 0.7g/l.

In the first Example, stoichiometric amounts of AgNO₃ solution are added with stirring, to the brine, at room temperature and at differing concentrations:

AgNO ₃ concn. (g/l)	150	200	600	918	1366
Volume added (ml)	87.6	65.7	21.6	14.5	9.5
Cl ⁻ concn. (g/l)	0.50	0.64	0.72-0.99	1.0	1.78
(all concentrations in g/l normalised to 200 ml)					
Specific gravity	1.848	1.913	2.084	2.117	2.129

In order to produce a product brine having Cl⁻ concentration of approximately 0.5g/l, combined with a specific gravity of not less than 2.0, a second stage treatment with AgNO₃ was undertaken, with the following results:

First stage product Cl ⁻ (g/l normalised)	0.99	1.00	1.78
AgNO ₃ stoichiometry (%)	50	50	80
AgNO ₃ concn. (g/l normalised)		200	90
200			
Final Cl ⁻ concn. (g/l normalised)	0.54	0.51	0.44
Overall AgNO ₃ stoichiometry (%)	103.2	103.4	110.0
Specific gravity	2.055	2.077	2.057

After first and second stages, the deposits formed in the brine were filtered off.

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EXAMPLE 2**Single Stage Chloride Removal**

The identical cesium formate brine as in Example 1 was used in further tests, using
5 differing stoichiometries:

Test No.	1	2	3
AgNO ₃ stoichiometry (%)	107	110	116
10 Vol. AgNO ₃ soln. added (ml)	10.2	10.4	11
Cl ⁻ concn. (g/l normalised)	0.58	0.35	<0.01
Specific gravity	2.111	2.122	2.095

Tests 1 and 2 proceeded satisfactorily at room temperature. It was assessed in Test 3 that
15 excess silver was being dissolved and a post-treatment of heating the product brine to 95°C was
incorporated, to remove the silver in solution.

A further post treatment of cooling to approximately 0°C overnight followed by
filtration, was found to remove a large proportion of by-product cesium nitrate, leaving a stable
20 clear solution at room temperature.

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CLAIMS

1. A method of treating an alkali metal carboxylate salt brine contaminated with chloride ion, comprising admixing such contaminated brine with a solution of a silver salt, especially silver nitrate, causing silver chloride to be formed in a reaction mixture and separating the silver chloride from the residual brine.

2. A method according to claim 1, wherein the brine comprises cesium as the alkali metal and formate, acetate or other species as the salt anion.

3. A method according to claim 1 or claim 2, comprising the use of a silver nitrate solution containing at least 950g/l AgNO_3 .

4. A method according to claim 1, 2 or 3, wherein by-product cesium nitrate is removed after cooling the reaction mixture, preferably to about 0°C.

5. A method according to any one of the preceding claims, wherein silver nitrate used in a quantity of from 105 to 115% of stoichiometric.

6. A method according to any one of the preceding claims, carried out such that the residual brine has a specific gravity of not less than 2.0.

7. A method of use of an alkali metal carboxylate salt brine, comprising the recovery of used brine contaminated with chloride ion, ~~treating the recovered brine with a solution of a~~ silver salt, especially silver nitrate, causing silver chloride to be formed, separating the silver chloride from the brine, and re-using the brine.

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IMPROVEMENTS IN METAL SALTS

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Abstract of the Disclosure

Alkali metal carboxylate salt brines, such as cesium formate brine, are used in oil and gas drilling procedures. Contamination with chloride ions can be controlled by treatment with a silver salt solution, and removing silver chloride formed. High density brines can be obtained, suitable for re-use.

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